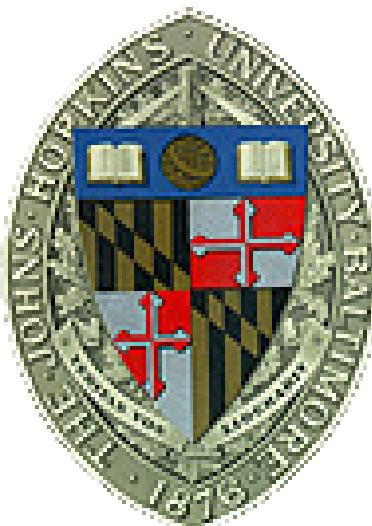


# Photodriven Molecule and Charge Transfer in Copper Donor-Acceptor Compounds



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ACS-PRF

NIH

## **A. Geometry Considerations**

- Cuprous and Cupric Oxidation States
  - MLCT Excited States

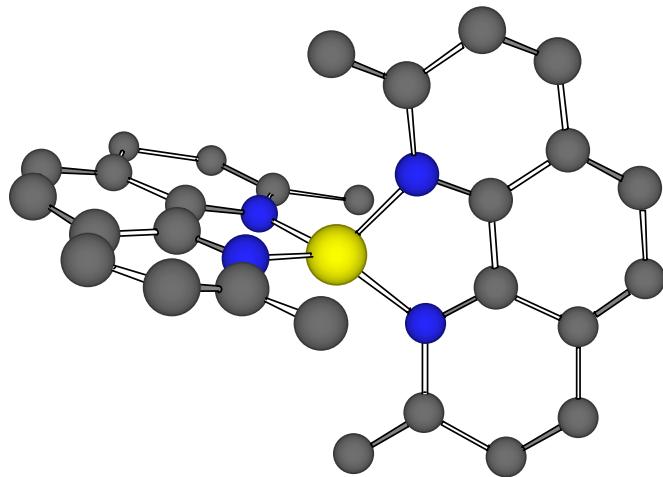
## **B. Long-Lived Photoluminescent Excited States**

- Quest for Long-Lived MLCT Excited States
- Crowded Cu(I) Compounds Based on 2,2'-bibenzo[h]quinoline

## **C. Excited State Electron Transfer**

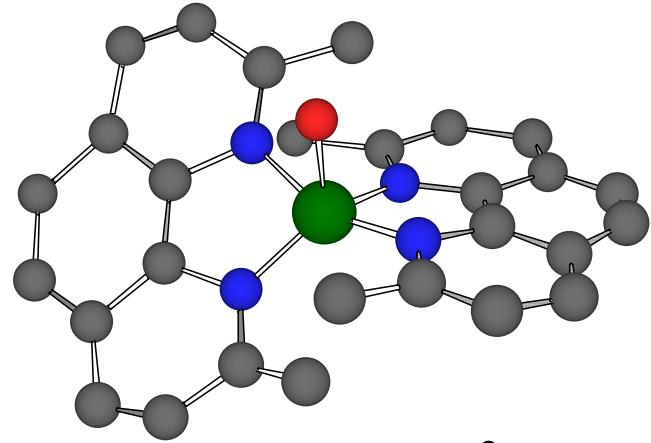
- Intramolecular Electron Transfer

# Geometry Considerations



$d^{10}$   
 $\text{CN} = 4$

Tetrahedral



$d^9$   
 $\text{CN} = 5$

Dis. Square Planar

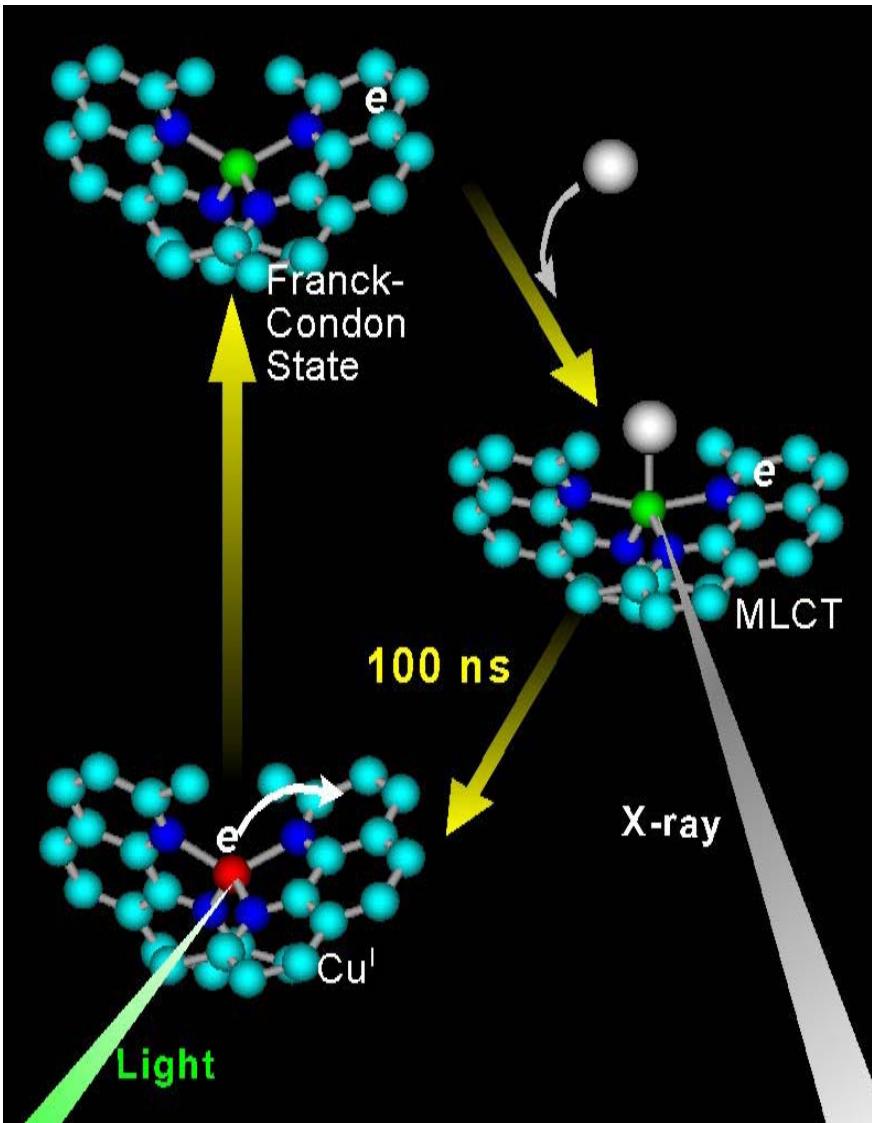
## MLCT Excited State?

Similar to Cupric State:

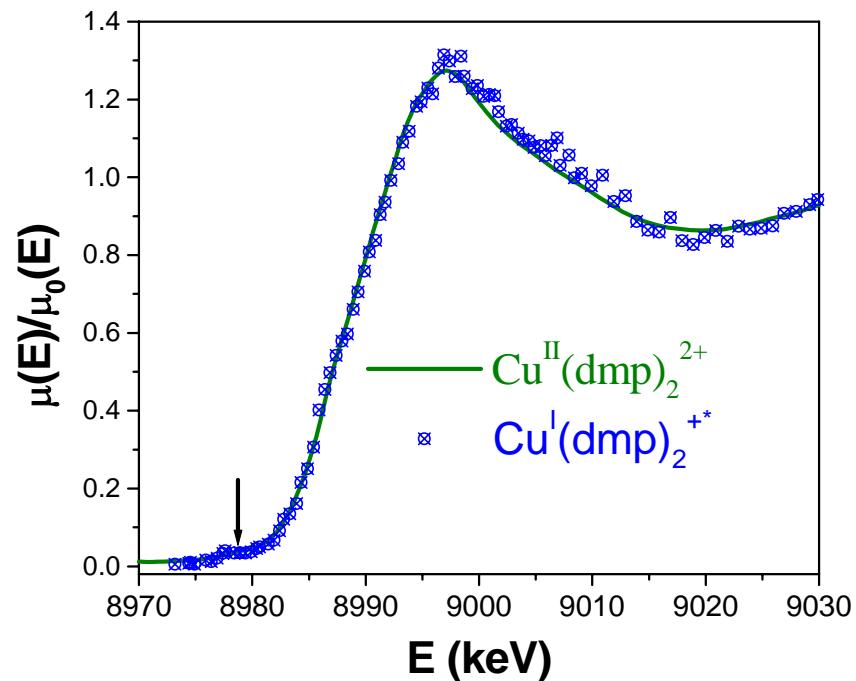
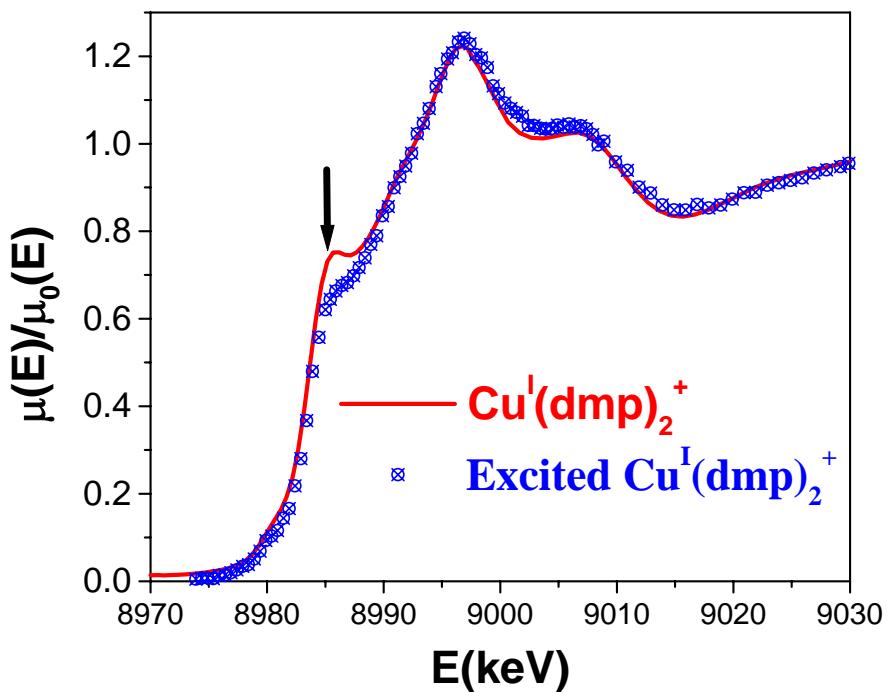
- 1) Formally Cu(II)
- 2) Large Stokes shift
- 3) Exciplex formation

# Nanosecond Pump Probe X-Ray

## Characterization of Cu(dmp)<sub>2</sub><sup>+</sup>\*

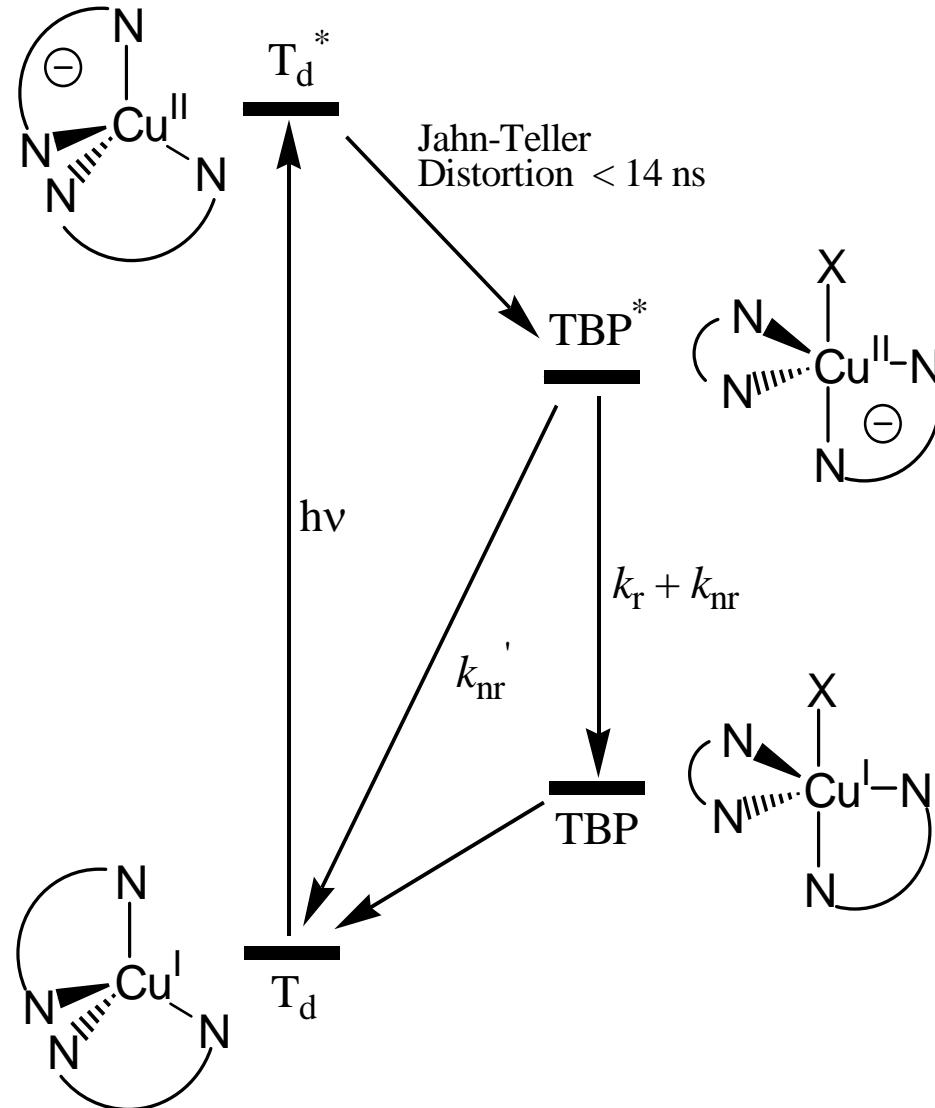


# Nanosecond Pump Probe XANES

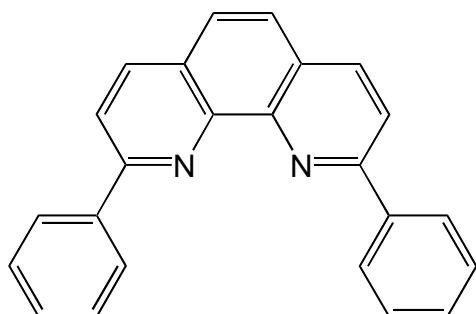


# Mechanism of Excited State Deactivation

*J. Am. Chem. Soc.* **2002**, *124*, 10861; *J. Am. Chem. Soc.* **2003**, *125*, 7022



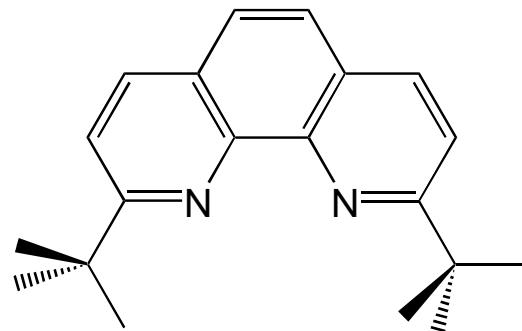
# The Quest for Long-Lived MLCT Excited States



$\tau = 280 \text{ ns}$

Sauvage et al.

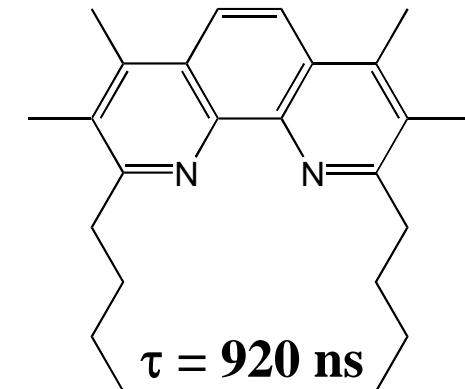
*Chem. Comm.* **1983**, 513.



$\tau = 730 \text{ ns}$

Karpishin et al.

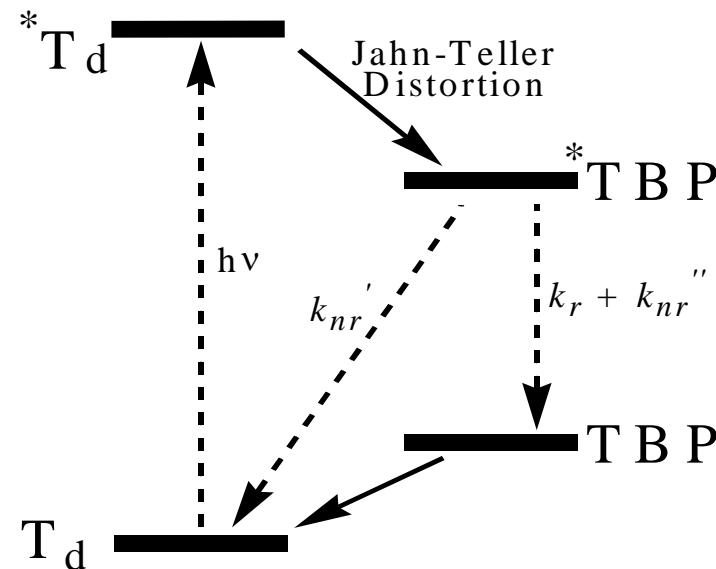
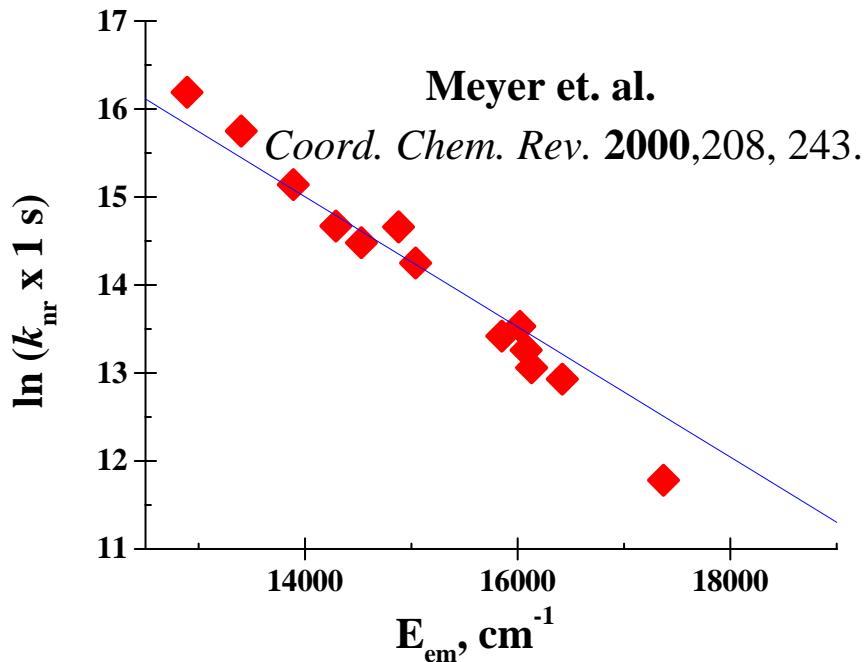
*JACS* **1999**, *121*, 4292.



$\tau = 920 \text{ ns}$

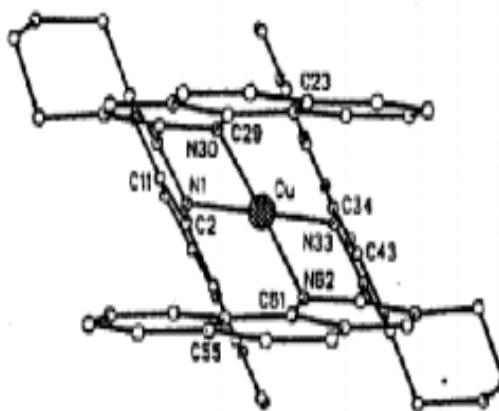
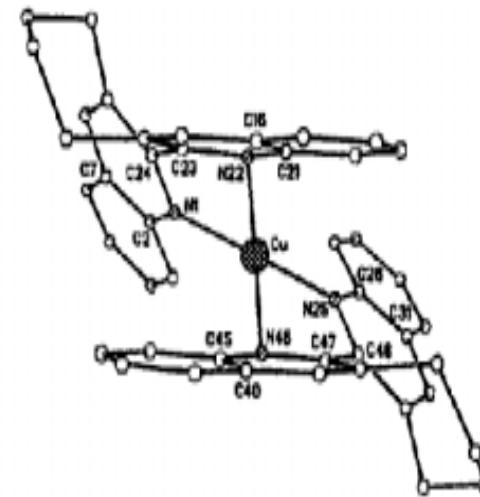
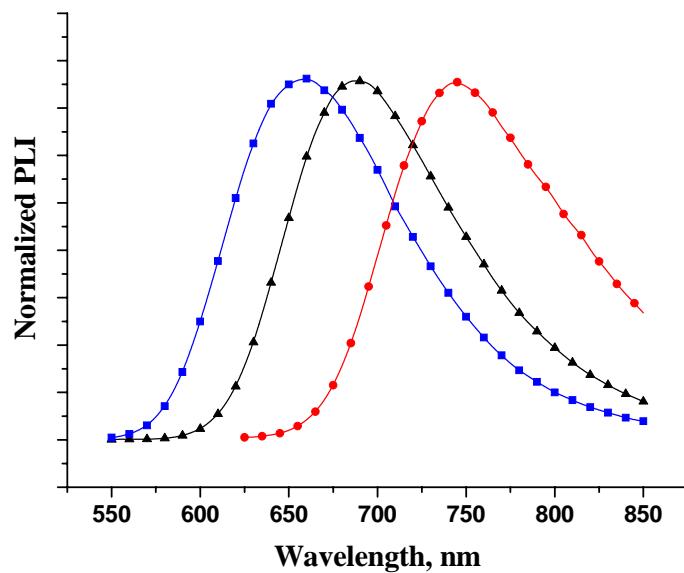
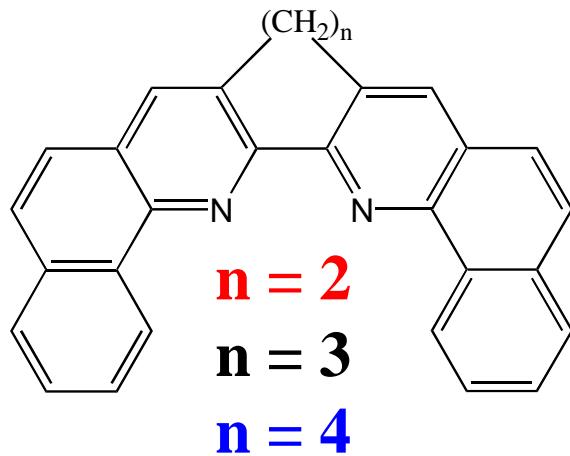
McMillin et al.

*IC* **1999**, *38*, 4388.

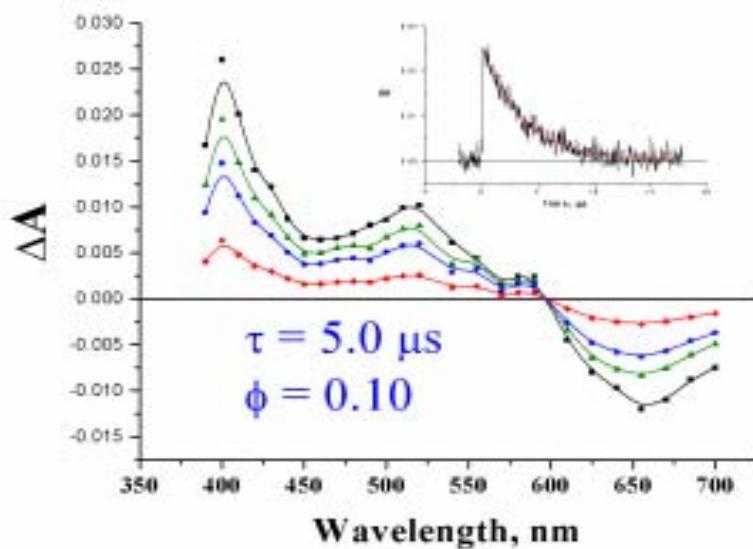
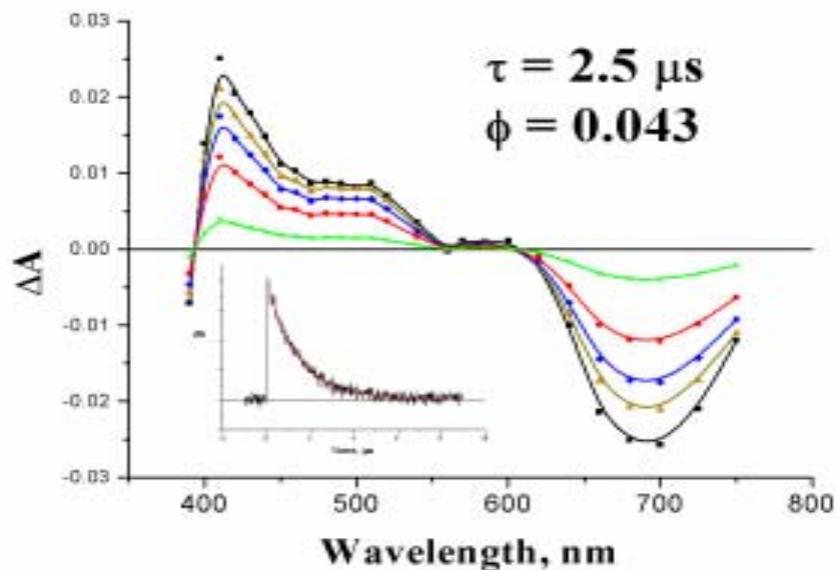
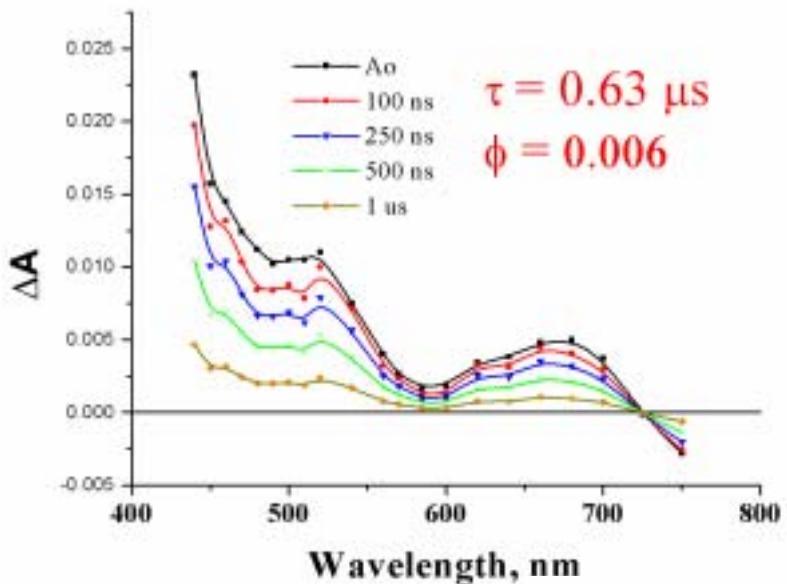


# Crowded Cu(I) Compounds

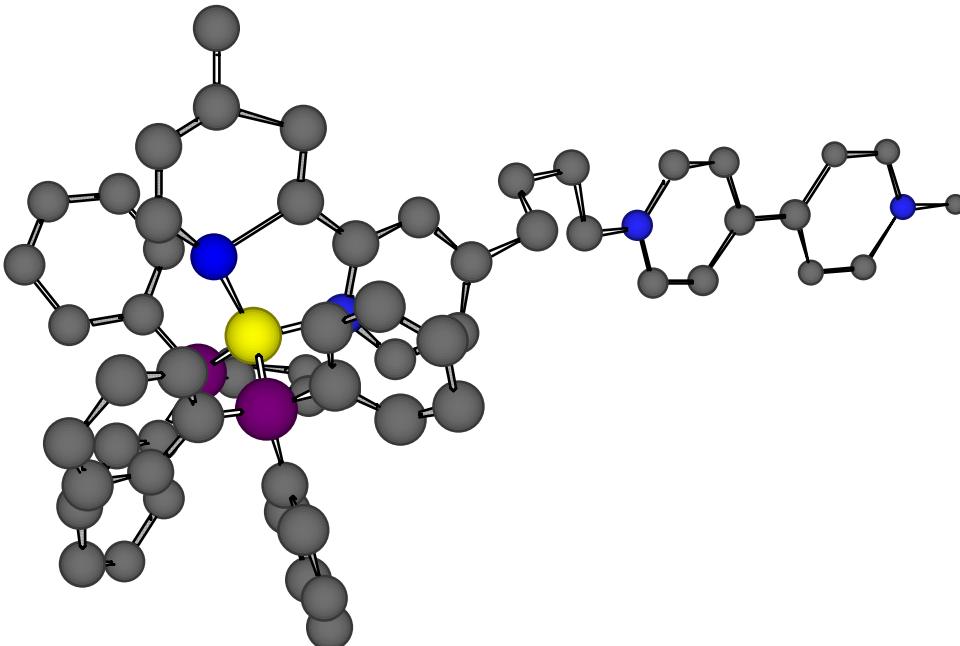
*Inorg. Chem.* 2001, **40**, 3413.



# Excited State Properties



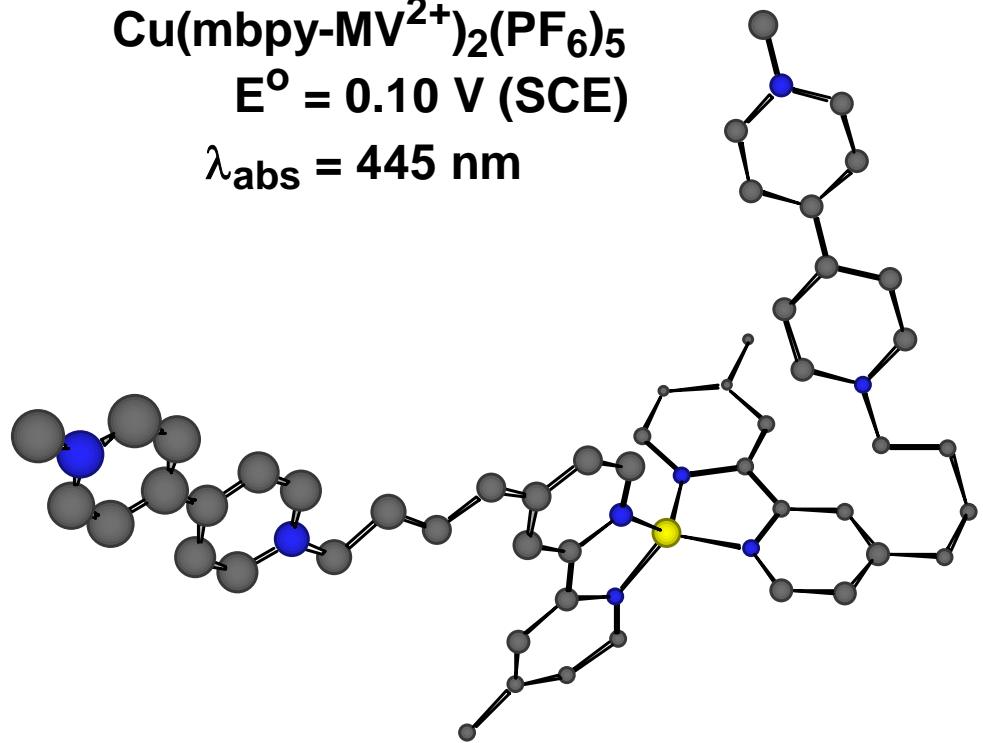
# Cuprous Donor Acceptor Compounds



**Cu(mbpy-MV<sup>2+</sup>)(PPh<sub>3</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>**  
 $E_{pa} \sim 0.7 \text{ V (SCE)}$   
 $\lambda_{abs} = 360 \text{ nm}$

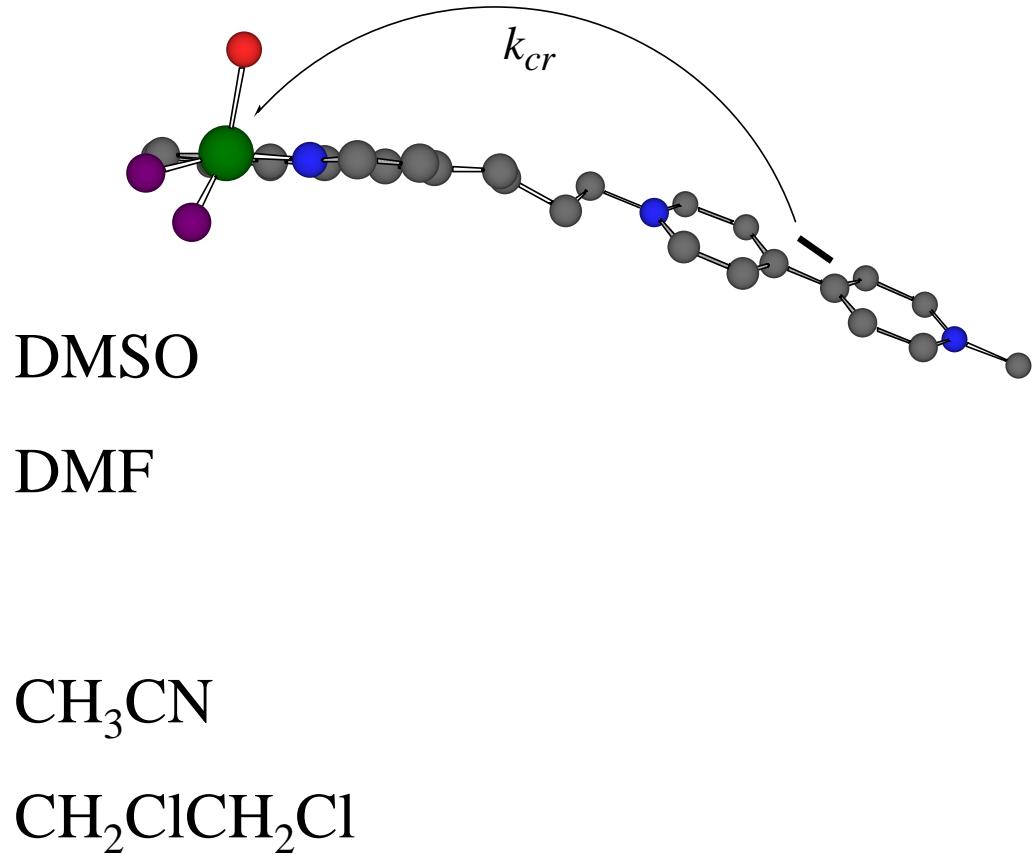
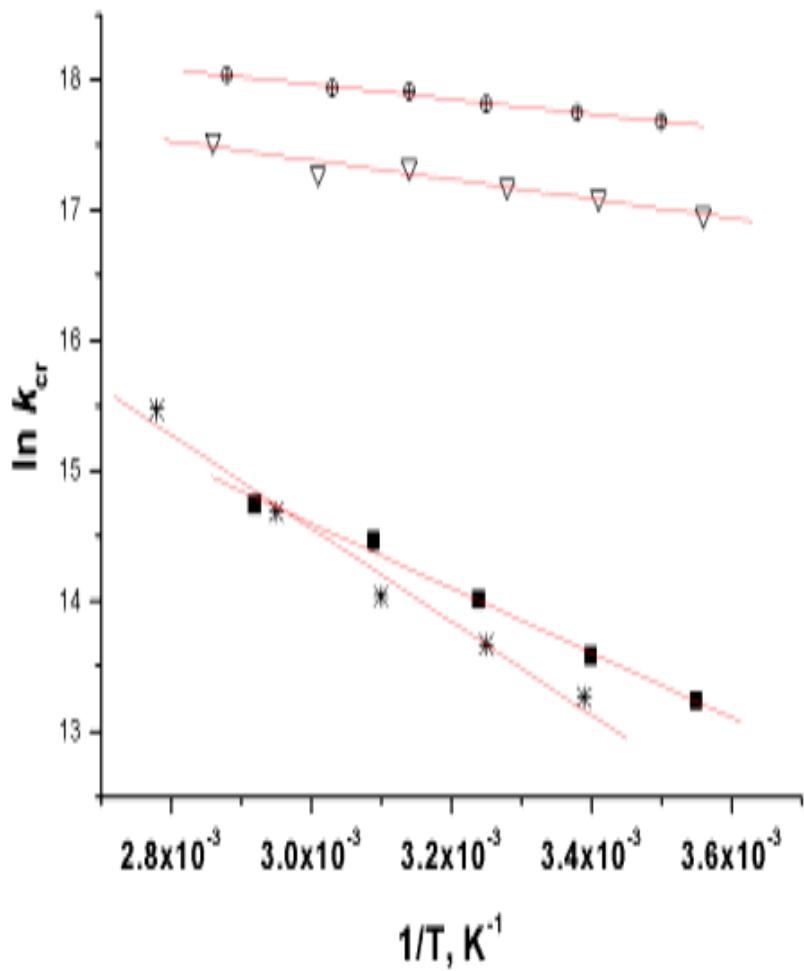
**CH<sub>2</sub>Cl<sub>2</sub>:**  $\lambda_{em} = 680 \text{ nm}$   
 $\tau = 90 \text{ ns}$

**Cu(mbpy-MV<sup>2+</sup>)<sub>2</sub>(PF<sub>6</sub>)<sub>5</sub>**  
 $E^\circ = 0.10 \text{ V (SCE)}$   
 $\lambda_{abs} = 445 \text{ nm}$



# Adduct Formation in the Charge Separated State?

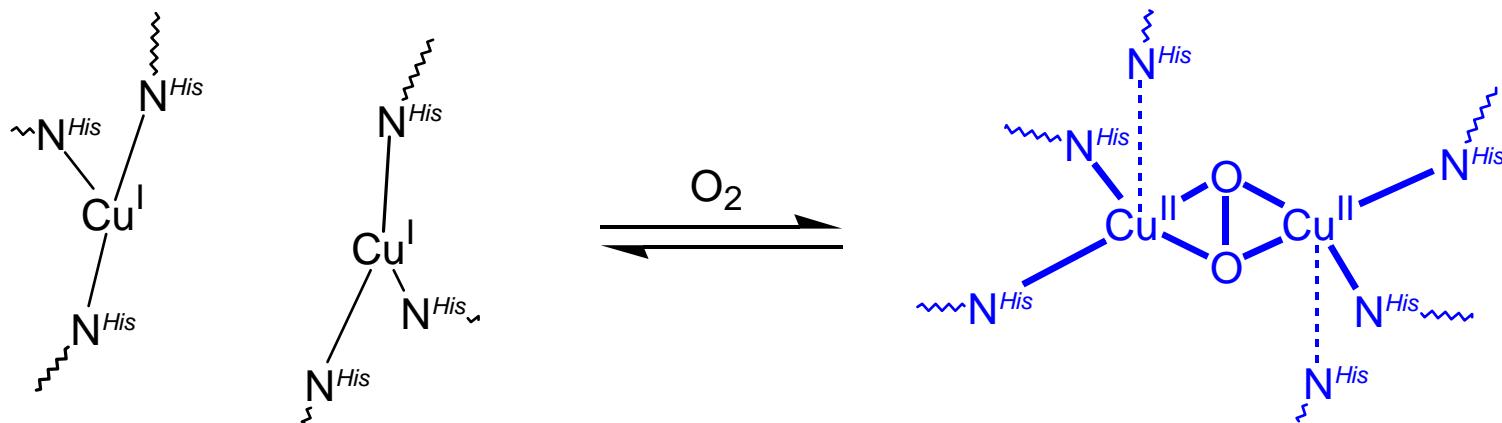
*J. Amer. Chem. Soc.* **1997**, *119*, 12004; *Inorg. Chem.* **2000**, *39*, 3777.



# Activation Energies for Charge Recombination

Solvent	$\Delta G \neq$ (kJ/mol)	$\Delta H \neq$ (kJ/mol)	$\Delta S \neq$ (J/K*mol)
CH <sub>2</sub> ClCH <sub>2</sub> Cl	<b>31 ± 4</b>	<b>2 ± 0.5</b>	<b>-90 ± 10</b>
CH <sub>3</sub> CN	<b>32 ± 4</b>	<b>4 ± 1</b>	<b>-90 ± 10</b>
DMF	<b>40 ± 3</b>	<b>18 ± 2</b>	<b>-70 ± 6</b>
DMSO	<b>39 ± 3</b>	<b>25 ± 3</b>	<b>-60 ± 6</b>

# Hemocyanin Active Site Structures



deoxy-Hemocyanin

colorless

oxy-Hemocyanin

blue

## Limulus II (horseshoe crab):

Cu...Cu = 4.6 Å

Trigonal-planar Cu(I), Cu-N ~ 2.0 Å

## Limulus II (horseshoe crab):

Cu...Cu = 3.6 Å

$\lambda_{\text{max}} = 345 (\varepsilon \sim 20,000)$ , 570 nm (1,000)

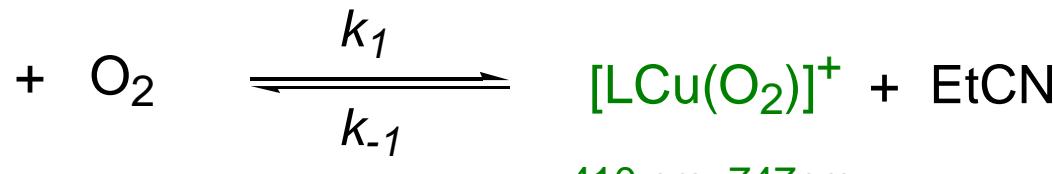
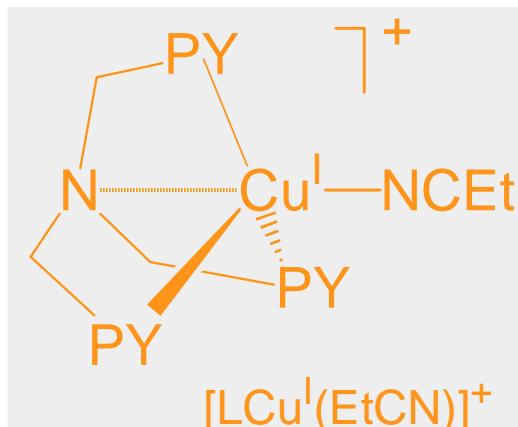
$\nu(\text{O-O}) \sim 750 \text{ cm}^{-1}$

Diamagnetic

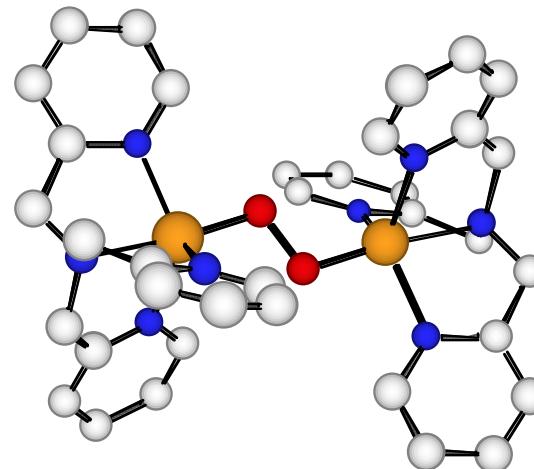
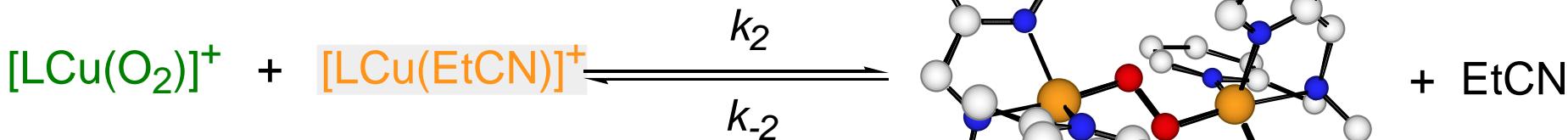
K. A. Magnus et al., *Proteins, Struct., Funct., Genet.*, 1994, 19, 302.

B. Hazes et al., *Protein Sci.*, 1993, 2, 597.

# Reversible O<sub>2</sub>-Binding of TMPA-Cu(I)

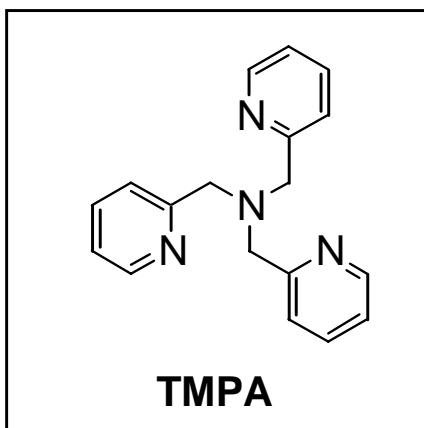


410 nm, 747 nm



[ $(LCu)_2(O_2)$ ]<sup>2+</sup>

525 nm  
595 nm (sh)



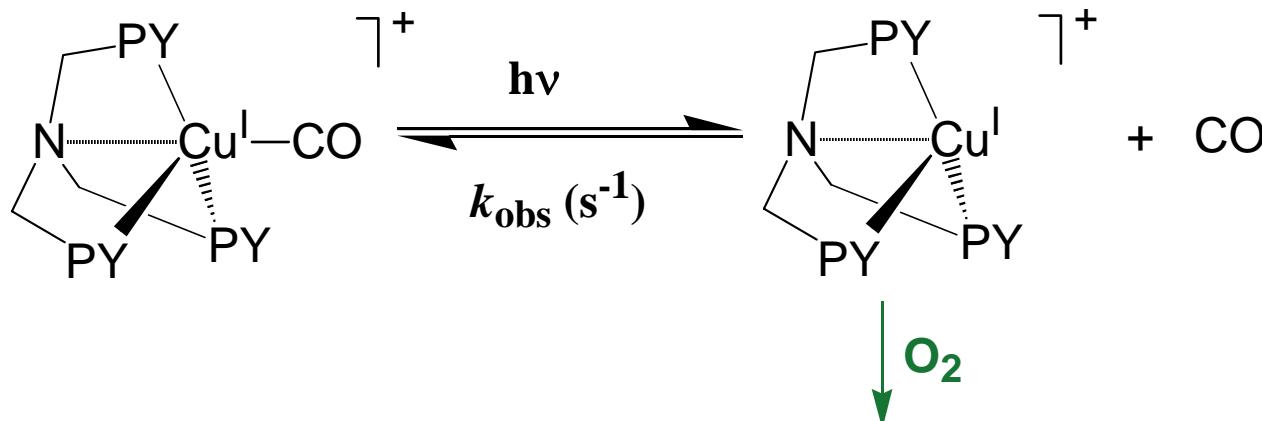
Karlin, Kaderli & Zuberbühler, Acc. Chem. Res., 1997, 30, 139-147

# Goal: Observe the Formation of $[(\text{TMPA})\text{Cu}^{\text{II}}(\text{O}_2^-)]^+$

'Flash and Trap'

Time Resolution: ns

Rely on CO Photolability

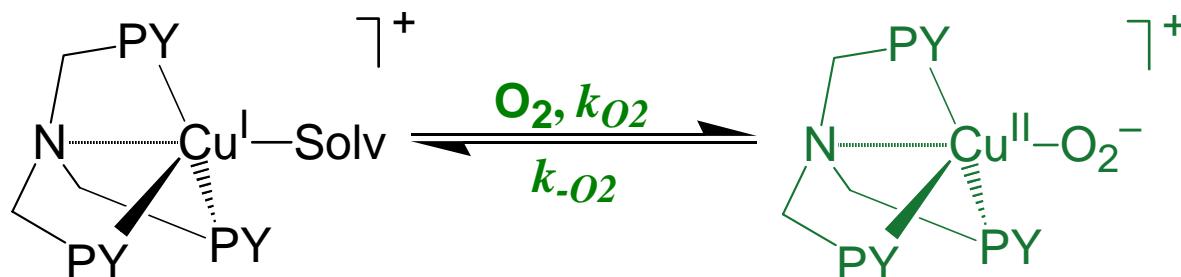


Stopped-Flow Kinetics

Time Resolution: ms

Directly Observe O<sub>2</sub> Binding

No CO Competition



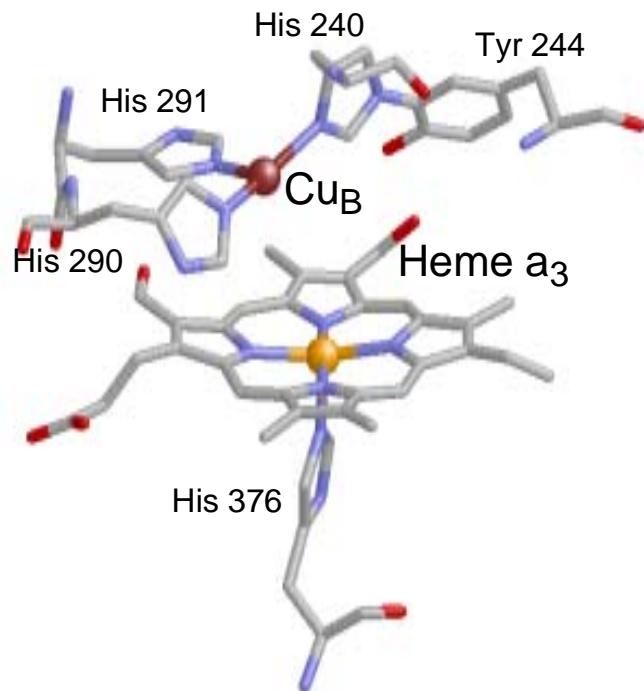
	Temp	$k_{\text{O}2} (\text{M}^{-1} \text{ s}^{-1})$	$K_{\text{O}2} (\text{M}^{-1})$	
EtCN	183 K	$1.18 \times 10^4$	$\Delta H^\ddagger = 31.6$ $\Delta S^\ddagger = 10$	740
	223 K	$5.0 \times 10^5$		22
	298 K	$5.8 \times 10^7$		0.38
THF	183 K	$\geq 2 \times 10^6$	$\Delta H^\ddagger = \dots$ $\Delta S^\ddagger = \dots$	$7 \times 10^5$
	223 K			$5.5 \times 10^3$
	298 K			$2.1 \times 10^1$

Units for  $\Delta H^\ddagger, \Delta H^\circ$ : kJ/mol

Units for  $\Delta S^\ddagger, \Delta S^\circ$ : J/mol K

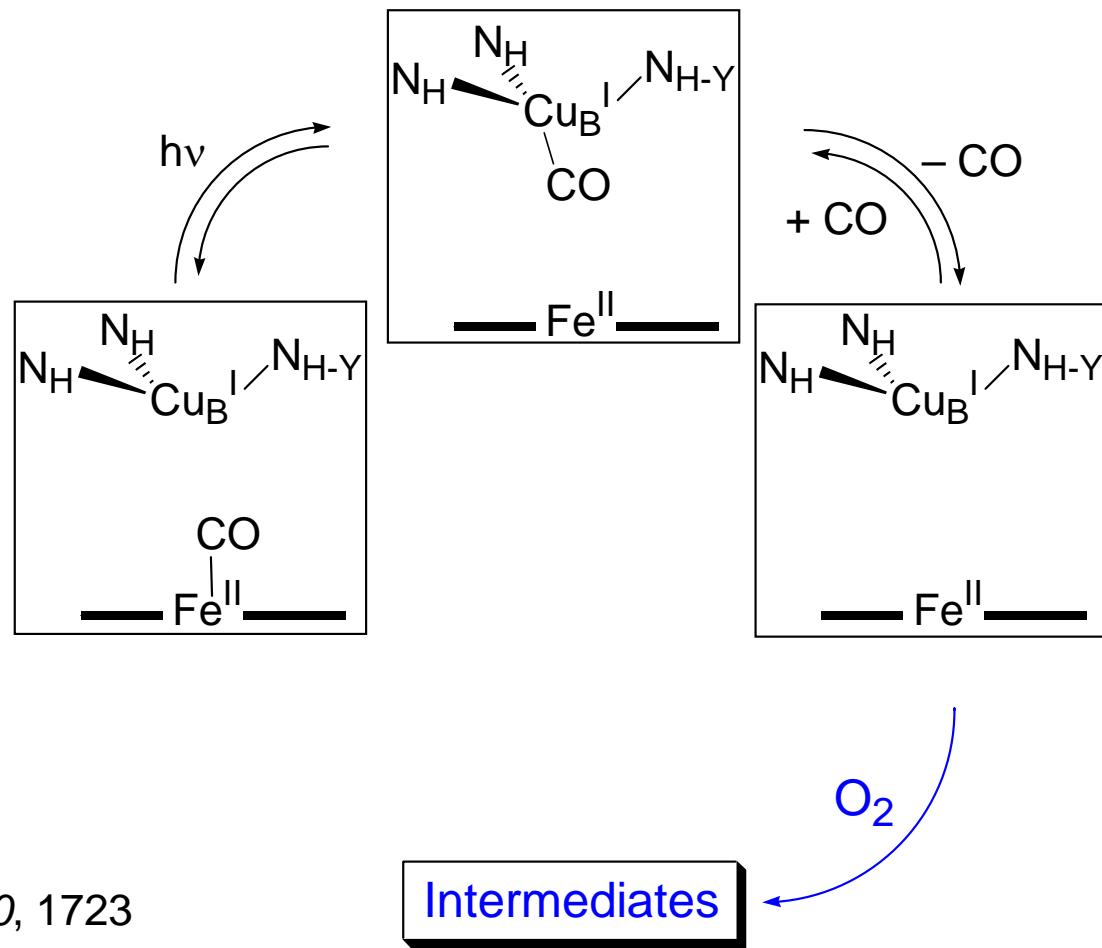
Inorg Chem., 2003, ASAP

# Use of CO Photolability in Cytochrome *c* Oxidase



$\text{Fe}^{\text{II}}\text{..Cu}^{\text{I}}$  distance : 5.19 Å

S. Yoshikawa *et al.* *Science*, 1998, 280, 1723

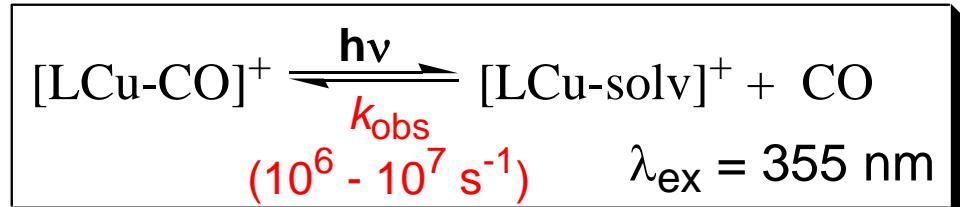
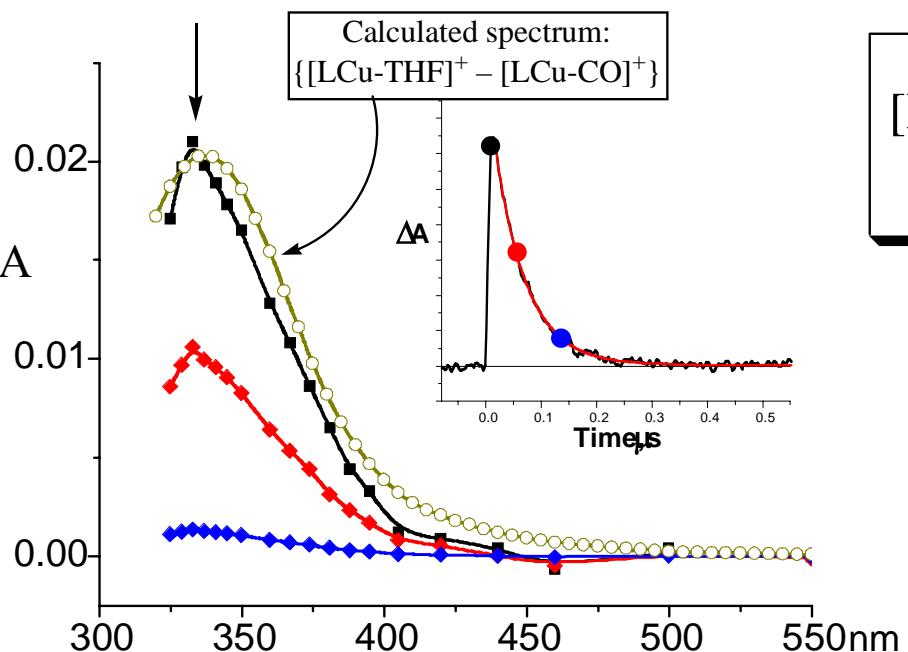


Greenwood, C.; Gibson, Q. H. J. *Biol. Chem.* 1967, 242, 1782-1787

Woodruff, W. H. et al. *Biochemistry* 1993, 32, 12013-12024

Paula, S.; Sucheta, A.; Szundi, I.; Einarsdóttir, Ó. *Biochemistry* 1999, 38, 3025-3033

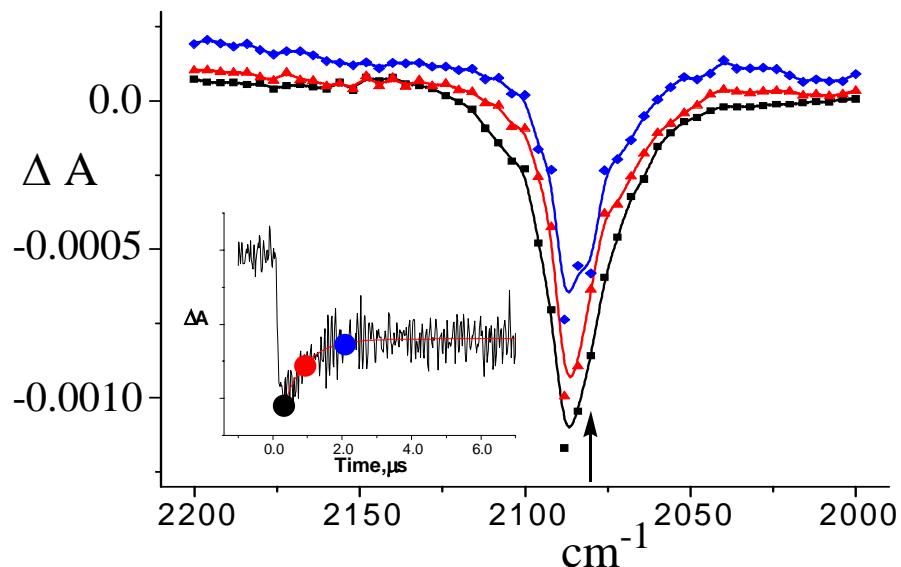
# Time-Resolved Spectroscopies



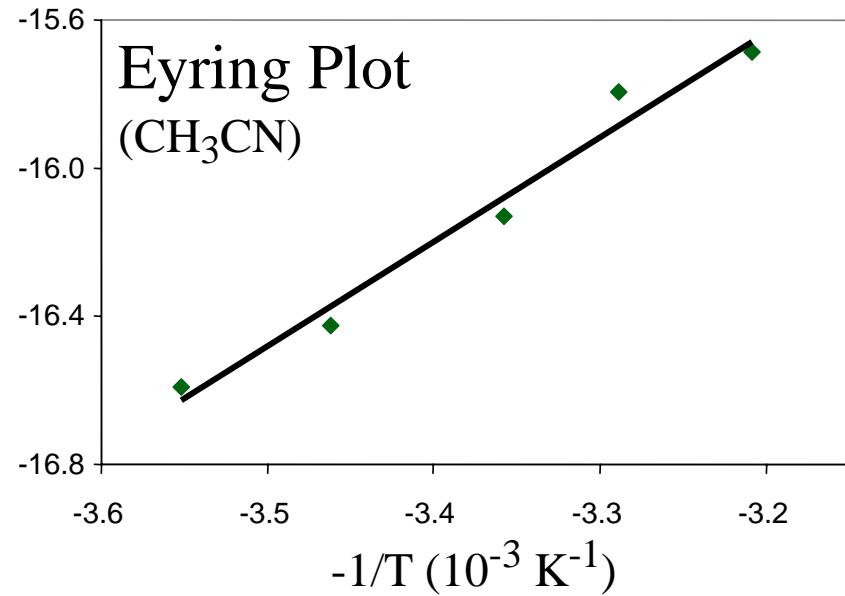
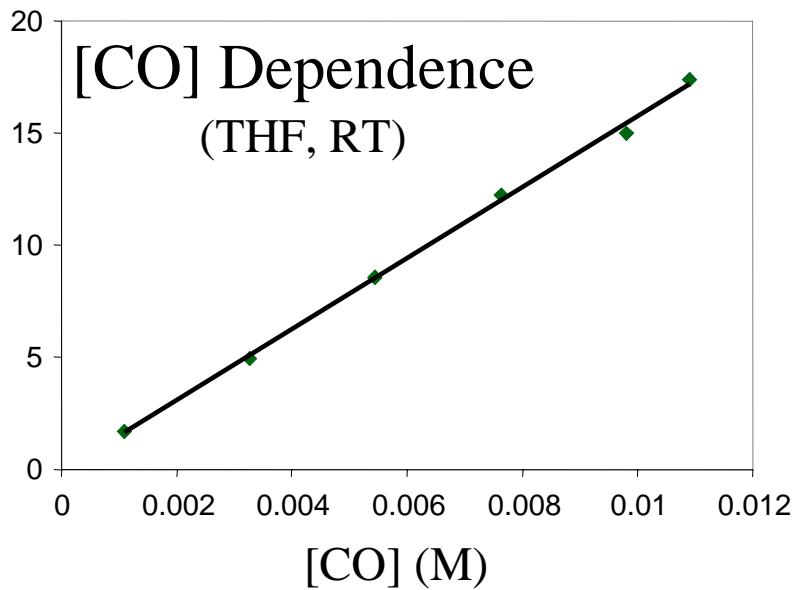
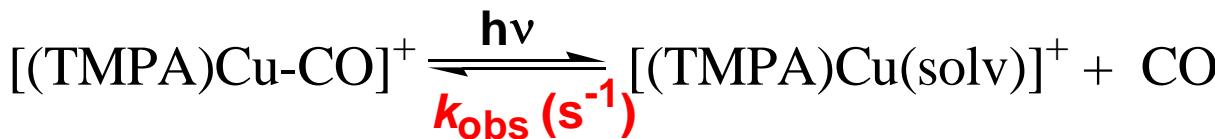
- $\Delta A$  plot: Formation of copper solvato species ( $t = 10 \text{ ns}$ ) and decay to the  $[\text{LCu-}\text{CO}]^+$  (baseline) in excess CO
- Inset: Pseudo first-order kinetic trace at  $\lambda_{\text{max}} = 333 \text{ nm}$ .

**TRIR:**  $\text{CH}_3\text{CN}$  solvent, RT, 1 atm CO

- $[(\text{TMPA})\text{Cu}(\text{CO})]^+$   $\nu_{\text{CO}}$ :  $2092 \text{ cm}^{-1}$
- Inset: Kinetics at  $\nu_{\text{CO}} = 2088 \text{ cm}^{-1}$

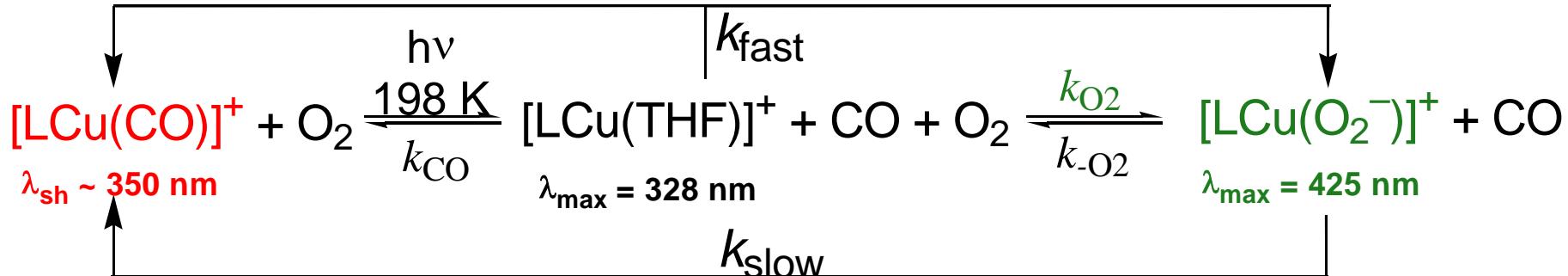


# Physical Analysis of CO Recombination

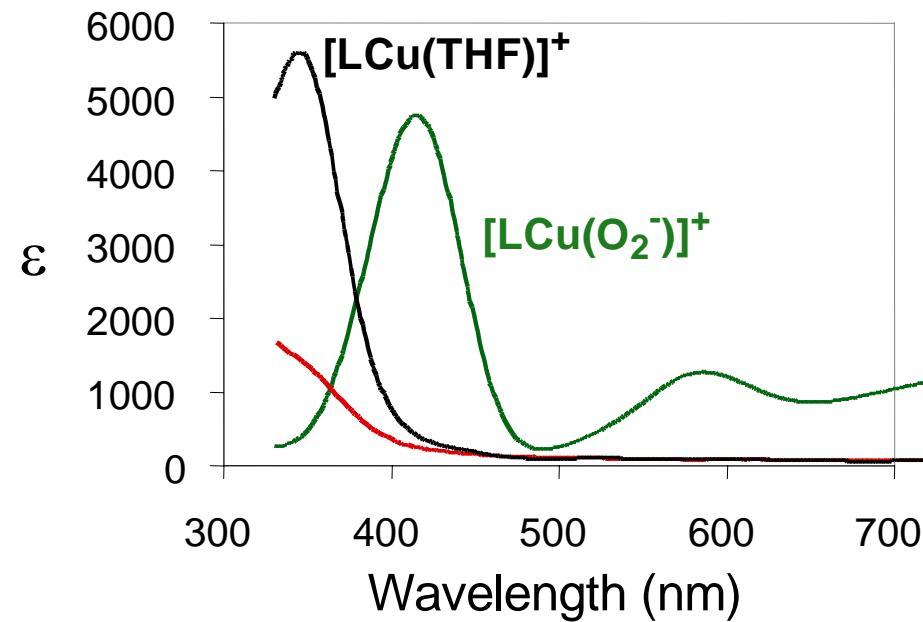


Solvent/ Temp	$k_{\text{CO}}$ (M <sup>-1</sup> s <sup>-1</sup> )	$\Delta G^\ddagger$ (298 K)	$\Delta H^\ddagger$	$\Delta S^\ddagger$
CH <sub>3</sub> CN (298 K)	$3.1 \times 10^7$	39.9 kJ/mol	22.3 kJ/mol	-59.5 J/mol K
THF (298 K)	$1.6 \times 10^9$	-----	-----	-----
THF (198 K)	$3.7 \times 10^8$	-----	-----	-----

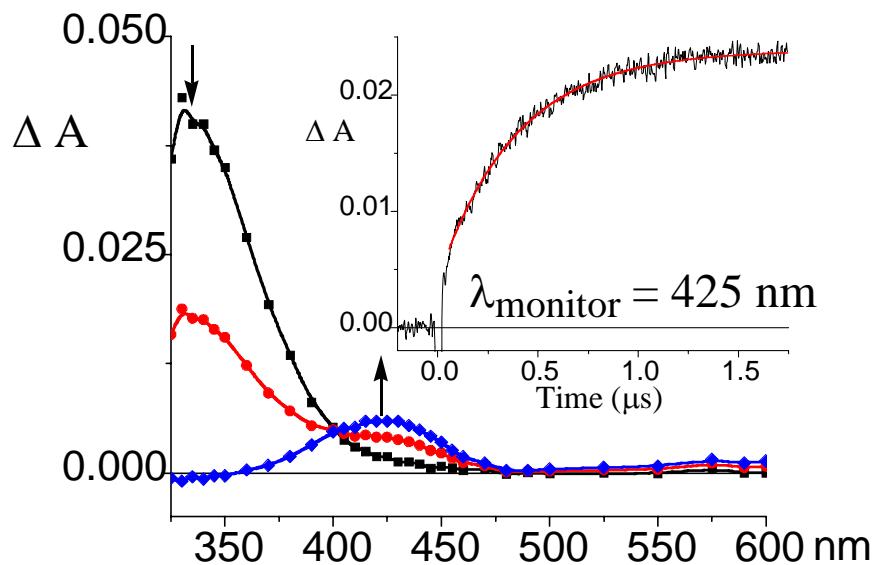
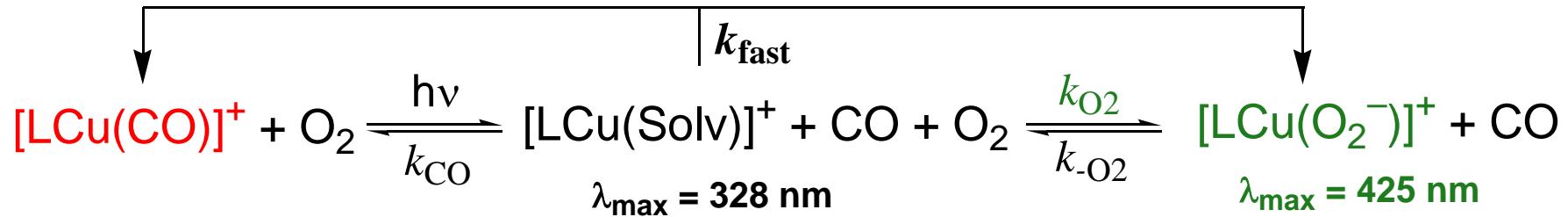
# Flash and Trap (198 K, THF) Observation of $[(\text{TMPA})\text{Cu}(\text{O}_2^-)]^+$



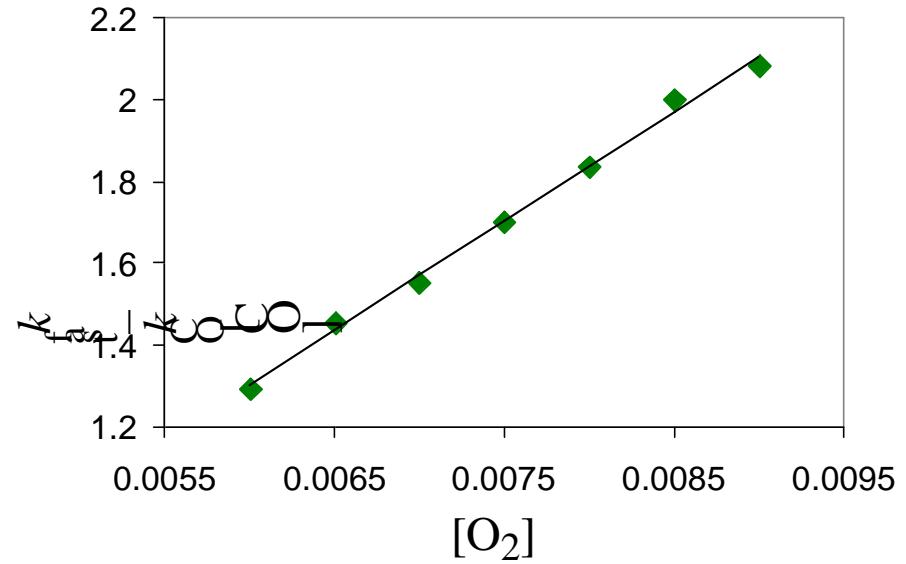
- CO 'protects'  $[\text{LCu}]^+$  from  $\text{O}_2$ -reactivity
- Photoexcitation of  $[\text{Cu}^{\text{I}}(\text{tmpa})(\text{CO})]^+$  in  $\text{CO}/\text{O}_2$  mixtures results in partial formation of  $[\text{Cu}^{\text{II}}(\text{tmpa})(\text{O}_2^-)]^+$
- $k_{\text{CO}} = 3.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$   
(THF, 198 K, 1 atm CO)
- $k_{\text{O}_2}$  and  $K_{\text{O}_2}$  can be determined



# Competitive Binding of O<sub>2</sub> and CO



- $\lambda_{excitation} = 355 \text{ nm}$
- Temp = 193-198 K
- [CO]:[O<sub>2</sub>] varied by gas flow control



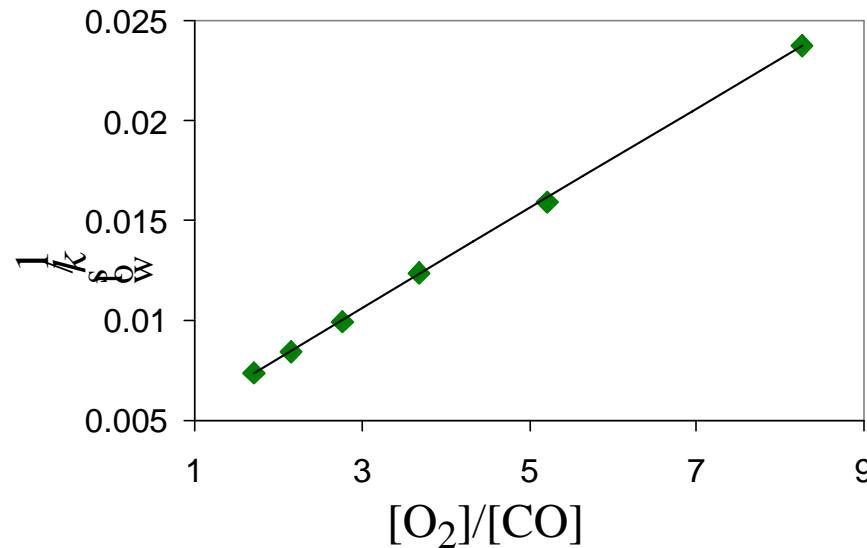
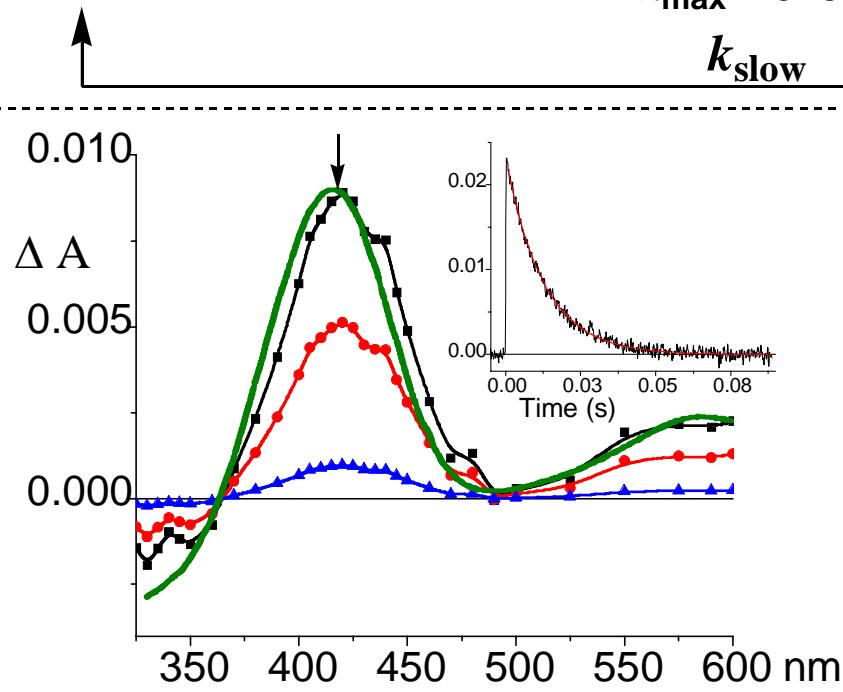
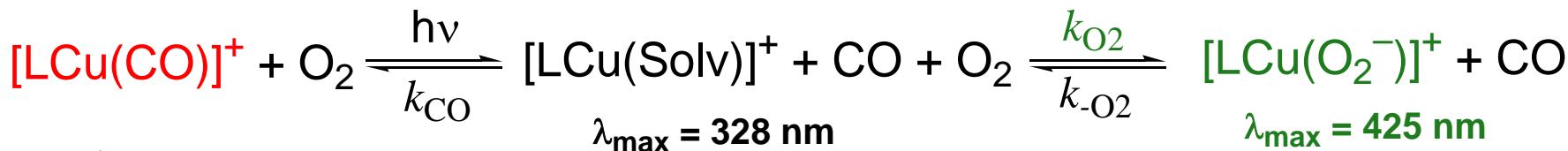
$$k_{fast} = k_{CO}[CO] + k_{-CO} + k_{O_2}[O_2] + k_{-O_2}$$

$$k_{fast} = k_{CO}[CO] + k_{O_2}[O_2]$$

$$k_{fast} - k_{CO}[CO] = k_{O_2}[O_2]$$

$k_{O_2} = 2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$

# Equilibration of $[(\text{TMPA})\text{Cu}(\text{O}_2^-)]^+$ to $[(\text{TMPA})\text{Cu}(\text{CO})]^+$



$$k_{\text{slow}} = \frac{k_{-\text{O}_2} k_{\text{CO}} [\text{CO}]}{k_{\text{O}_2} [\text{O}_2] + k_{-\text{O}_2} + k_{\text{CO}} [\text{CO}] + k_{-\text{CO}}}$$

$$\frac{1}{k_{\text{slow}}} = \frac{K_{\text{O}_2} [\text{O}_2]}{k_{\text{CO}} [\text{CO}]} + \frac{1}{k_{-\text{O}_2}}$$

$$K_{\text{O}_2} = 7.5 \times 10^5 \text{ M}^{-1}$$

$$k_{-\text{O}_2} = 330 \text{ s}^{-1}$$

$$k_{\text{O}_2} = 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Antonini, E.; Brunori, M. *Hemoglobin and Myoglobin in Their Reactions with Ligands*; North-Holland Publishing Co.; Amsterdam, 1971.

# Rate Constants for Hemes & Copper Proteins and Complexes

Protein / Complex	$k_{O_2} (M^{-1} s^{-1})$	$k_{-O_2} (s^{-1})$
Durene-Capped Heme	$0.98 - 10 \times 10^7$	$10^4 - 10^5$
Picket Fence and Pocket Heme	$0.2 - 43 \times 10^7$	$9 - 2900$
Mb (Sperm whale, E7 His)	$1.4 \times 10^7$	12
Mb (Sperm whale, E7 Gly)	$14.0 \times 10^7$	1600
Mb (Range of Mutant and WT)	$0.88 - 25.0 \times 10^7$	$12 - 23000$
Hb ( $\alpha$ -chain, Human)	$3.36 \times 10^7$	28
Hemocyanin	$0.5 - 5.7 \times 10^7$	$60 - 1000$
Tyrosinase	$2.3 \times 10^7$	1070
CcO ( $Fe_{a3}$ )	$1.1 \times 10^8$	N. A.
CcO ( $Fe_{a3}$ )	$9.0 \times 10^4 s^{-1}$	N. A.
CcO ( $Cu_B$ )	$3.5 \times 10^8$	$5 \times 10^4$
$[(TMPA)Cu(EtCN)]^+ (198 K, EtCN)$	$6.3 \times 10^4$	270
$[(TMPA)Cu(THF)]^+ (198 K, THF)$	<b><math>2.5 \times 10^8</math></b>	<b>300</b>

- Changing the solvent from EtCN to THF increases  $k_{O_2}$  by  $> 10^3 M^{-1} s^{-1}$ .
- $O_2$ -binding ( $k_{O_2}$ ) to  $[(TMPA)Cu(THF)]^+$  exceeds that for Cu-proteins and hemes.
- Insight to the possible role of  $Cu_B$  in CcO as a 'way stop' for  $O_2$ -binding?

# Conclusions

- Excited state structural determination by x-rays realized for the first time.
- Non-radiative decay from Cu MLCT excited state follows the energy gap law.
- Long-lived emissive Cu excited states achieved through minimizing excited state distortion and pi-stacking.
- Evidence for controlling charge separation lifetimes in Cu D-A compounds through inner-sphere coordination.
- Photodissociation of CO allows rapid kinetics for O<sub>2</sub> binding to copper to be quantified for the first time.